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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. Mo-5400/RC-204
First Inventor or Application Identifier Ludger Heiliger
Title Process for the Production of ...
Express Mail Label No. EK243943356US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 12] 1
(preferred arrangement set forth below)
- Descriptive title of the Invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure
3. ☐ Drawing(s) (35 U.S.C. 113) [Total Sheets ☐]
4. Oath or Declaration [Total Pages 2] 1
a. ☒ Newly executed (original or copy)
b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 16 completed)
i. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting
inventor(s) named in the prior application,
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

* NOTE FOR ITEMS 1 & 13 IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY
FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT
IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
a. ☐ Computer Readable Copy
b. ☐ Paper Copy (identical to computer copy)
c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement of Power of Attorney
(when there is an assignee)
9. ☐ English Translation Document (if applicable)
10. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☒ Copies of IDS Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
13. ☐ Small Entity Statement filed in prior application
Statement(s) Status still proper and desired
(PTO/SB/09-12)
14. ☒ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
15. ☐ Other: _____

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP)

of prior application No. _____

Prior application information: Examiner _____

Group / Art Unit: _____

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

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**PROCESS FOR THE PRODUCTION OF DITHIOPHOSPHORIC ACID
POLYSULFIDE MIXTURES**

FIELD OF THE INVENTION

5

This invention relates to a novel process for the production of dithiophosphoric acid polysulfide mixtures starting from dithiophosphoric acid disulfide.

BACKGROUND OF THE INVENTION

10

Dithiophosphoric acid polysulfides are known, as is the use thereof as vulcanizing agents or vulcanizing accelerators for the vulcanization of rubber (*c.f.* DE 19 36 694, DE 22 49 090 and DE 44 31 727). Dithiophosphoric acid polysulfides may be produced from the corresponding dithiophosphoric acids or the alkali metal salts thereof and sulfur chlorides, such as disulfur dichloride or sulfur dichloride.

15

The disadvantages of reacting dithiophosphoric acids with sulfur chlorides include the elevated corrosiveness of the sulfur chlorides and the unpleasant odor thereof, which gives rise to handling problems and entails appropriate, complex plant and equipment. According to EP 0 383 102 A1, sulfur dichloride, moreover, very readily disproportionates, such that dithiophosphoric acid trisulfides are not directly obtainable using this process.

20

Additionally, the dithiophosphoric acid tetrasulfides obtained using the process described above have a tendency, due to the low stability thereof, to eliminate sulfur. In order to prevent this, it is necessary to stabilize the dithiophosphoric acid tetrachlorides against sulfur precipitation as is described, for example, in DE 44 31 727.


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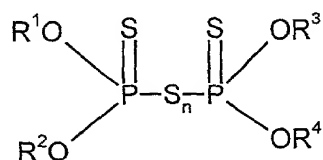

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SUMMARY OF THE INVENTION

The object of the present invention is accordingly to provide a process for the production of dithiophosphoric acid polysulfide mixtures which avoids the use of sulfur chlorides and gives rise to sulfur-stable dithiophosphoric acid polysulfide mixtures.

DETAILED DESCRIPTION OF THE INVENTION

The present invention accordingly provides a process for the production of dithiophosphoric acid polysulfide mixtures of the formula

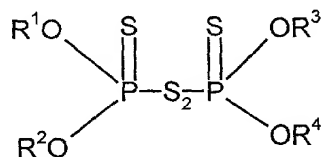


in which

R^1 to R^4 are identical or different and denote a linear or branched C_1 - C_{18} alkyl residue, C_1 - C_{18} alkenyl residue, C_5 - C_{28} cycloalkyl residue, C_5 - C_{28} cycloalkenyl residue as well as a C_6 - C_{28} aryl residues or C_7 - C_{28} aralkyl residue and

n denotes a number from 2.5 to 3.5,

which is characterized in that dithiophosphoric acid disulfides of the formula



in which

R¹ to R⁴ have the above-stated meaning,

5 are reacted with 0.5 to 1.5 mol of sulfur, optionally in the presence of a solvent, at temperatures of 100 to 140°C.

The numeric values for n are determined statistically in accordance with the sulfur chain distribution in the molecule.

10 The residues R¹ to R⁴ of the above-stated formulae may be substituted by suitable residues which are not disruptive to the subsequent use of the polysulfides, wherein alkyl residues and cycloalkyl residues may, in particular, be mentioned.

15 Preferred residues R¹ to R⁴ are C₆-C₁₂ alkyl residues, in particular C₈-C₁₂ alkyl residues, in particular branched alkyl residues, such as 2-ethylhexyl.

The dithiophosphoric acid polysulfide mixtures produced according to the invention are preferably those in which n denotes numbers from 2.8 to 3.3.

20 The dithiophosphoric acid disulfides to be used in the process according to the invention are also known and are described, for example, in the *Journal of Applied Polymer Science*, volume 19, pp. 865-877 (1975). The disulfides are produced, for example, by oxidizing dithiophosphoric acid with hydrogen peroxide or HOCl or a mixture of potassium bromide and hydrogen peroxide.

25 In the process according to the present invention, the disulfides used are preferably reacted with 0.8 to 1.3 mol of elemental sulfur, wherein temperatures of 110 to 130°C, in particular of 120 to 130°C, are preferred.

30 If the reaction is to be performed in solution, the solvents used are in particular aliphatic solvents, for example naphtha, aromatic solvents, for example toluene, or

halogenated aromatic solvents, such as chlorobenzene. The solvents may, of course, also be used as a mixture with each other.

5 The quantity of solvent may readily be determined by appropriate preliminary testing. Conventional quantities of solvent are from 0.1 to 50 wt.%, relative to the weight of the disulfide used.

10 It is furthermore possible to add hydrogen peroxide to the reaction according to the invention in order to prevent any possible color changes. In this case, the hydrogen peroxide is used in quantities of 0.1% to 5 wt.%, relative to the weight of the disulfide used.

15 Depending upon the reaction conditions employed, the reaction time ranges from approx. 10 minutes to approx. 6 hours.

20 Since the dithiophosphoric acid polysulfides produced according to the present invention are particularly sulfur-stable, i.e., they have no tendency to precipitate sulfur crystals, they are particularly suitable for use as sulfur donors for the vulcanization of natural and synthetic rubbers and for latex vulcanization of natural and synthetic rubber latex.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

Example 1

5 999.0 g (2.6179 mol) of O,O-di-2-ethylhexyldithiophosphoric acid diester (C₈-DTPS) having an acid value of 147 mg of KOH/g and 1.0 g (0.0084 mol) of potassium bromide are initially introduced at room temperature into a flask equipped with a stirrer, dropping funnel, gas inlet and reflux condenser and adjusted to a temperature of 30°C.

10

163.2 g (1.4399 mol) of hydrogen peroxide are then added dropwise in such a manner that the temperature in this strongly exothermic reaction does not rise above 40°C ± 5°C.

15

In order to accelerate phase separation, 50 g of naphtha (80-110) and 10 g of sodium chloride are added and the batch left to stand at 40°C ± 5°C until the phases have cleanly separated.

20

The bottom aqueous phase is separated. The yellow, turbid organic phase is heated to 70°C ± 5°C and distilled under a vacuum (20 to 60 mbar). The phase is then filtered through 1% diatomaceous earth.

25

For the second stage of the reaction, the batch is perfused with nitrogen for 5 minutes. Then 46.1 g (1.4399 mol) of sulfur are added and the reaction mixture heated to 122°C ± 2°C in order to boil down the sulfur. The batch is stirred for 4 hours at this temperature.

30

The yellow product may then be packaged without filtration. Even after several months' storage, the product exhibits neither turbidity nor precipitates.

The chain distribution in the resultant dithiophosphoric acid polysulfide mixture was determined by high pressure liquid chromatography (HPLC) as is as follows:

n = 1	0.8%	n = 4	19.9%	n = 72.5%, in reach case relative to the area of the HPLC signals
n = 2	29.2%	n = 5	8.1%	
n = 3	35.5%	n = 6	4.4%	

5 Example 2 (Comparative Example 1)

6000 g (15 mol) of O,O-di-2-ethylhexyldithiophosphoric acid diester (C₈-DTPS) having an acid value of 139.8 mg of KOH/g and 300 g of naphtha 80-100 are initially introduced into a vessel at room temperature. 2553.2 g of 23.5% sodium hydroxide solution (15.0 mol) are added within 1.5 h, wherein the temperature rises to 45°C. The temperature is then raised to 55°C in order subsequently to add 1003 g (7.4 mol) of S₂-Cl₂ dropwise within 5 h. The mixture is stirred for a further 30 minutes in order to take the reaction to completion.

15 The batch is then adjusted to pH 7 with approx. 600 g of 8% NaHCO₃ solution. In order to achieve good phase separation, the temperature is raised to 65°C and 1200 g of water are added.

20 Once the aqueous phase has been separated, the product is distilled for 3 h at 70°C under a water-jet vacuum. The product is then filtered, using a filtration auxiliary, through a heated vacuum filter. The product forms yellow crystalline precipitates after only a few hours, which prove to be elemental sulfur.

Example 3 (Comparative Example 2)

25

6000 g (15 mol) of O,O-di-2-ethylhexyldithiophosphoric acid diester (C₈-DTPS) having an acid value of 139.8 mg of KOH/g and 300 g of naphtha 80-100 are initially

introduced into a vessel at room temperature. 2553.2 g of 23.5% sodium hydroxide solution (15.0 mol) are added within 1.5 h, wherein the temperature rises to 45°C. The temperature is then raised to 55°C in order to subsequently add 1003 g (7.4 mol) of S₂-Cl₂ dropwise within 5 h. The mixture is stirred for a further 30 minutes in order to take the reaction to completion.

The batch is then adjusted to pH 7 with approx. 600 g of 8% NaHCO₃ solution. In order to achieve good phase separation, the temperature is raised to 65°C and 1200 g of water are added.

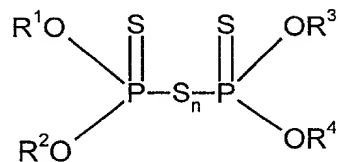
Once the aqueous phase has been separated, 282 g of 2-ethylhexanoic acid and 180 g of zinc oxide are added in portions at 65°C in order to provide stabilization against sulfur precipitation. Once addition is complete, the reaction is continued for a further 2 h at 70°C.

The product is dried by distilling it for 3 h at 70°C under a water-jet vacuum. The product is then filtered, using a filtration auxiliary, through a heated vacuum filter. The product forms yellow crystalline precipitates after only a few days, which prove to be elemental sulfur.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A process for the production of dithiophosphoric acid polysulfide mixtures of the formula



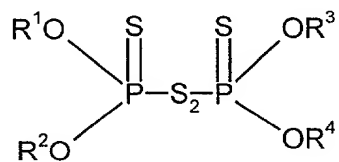
in which

R^1 to R^4 are identical or different and denote a linear or branched C_1 - C_{18} alkyl residue, C_1 - C_{18} alkenyl residue, C_5 - C_{28} cycloalkyl residue, C_5 - C_{28} cycloalkenyl residue as well as a C_6 - C_{28} aryl residue or C_7 - C_{28} aralkyl residue

and

n denotes a number from 2.5 to 3.5,

comprising the step of reacting dithiophosphoric acid disulfides of the formula

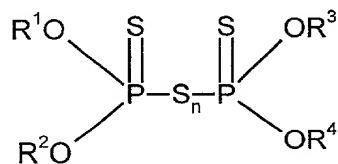


in which

R^1 to R^4 have the above-stated meaning,

with 0.5 to 1.5 mol of sulfur, optionally in the presence of a solvent, at temperatures of 100 to 140°C.

2. A sulfur donor for the vulcanization of natural and synthetic rubber comprising dithiophosphoric acid polysulfide mixtures of the formula



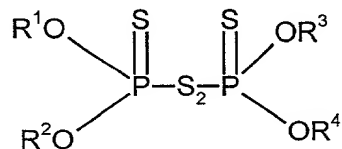
in which

R¹ to R⁴ are identical or different and denote a linear or branched C₁-C₁₈ alkyl residue, C₁-C₁₈ alkenyl residue, C₅-C₂₈ cycloalkyl residue, C₅-C₂₈ cycloalkenyl residue as well as a C₆-C₂₈ aryl residue or C₇-C₂₈ aralkyl residue

and

n denotes a number from 2.5 to 3.5,

wherein said dithiophosphoric acid polysulfide mixture is produced by reacting dithiophosphoric acid disulfides of the formula

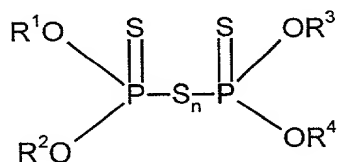


in which

R¹ to R⁴ have the above-stated meaning,

with 0.5 to 1.5 mol of sulfur, optionally in the presence of a solvent, at temperatures of 100 to 140°C.

3. A sulfur donors for the latex vulcanization of natural and synthetic rubber latex comprising dithiophosphoric acid polysulfide mixtures of the formula



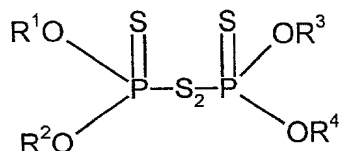
in which

R¹ to R⁴ are identical or different and denote a linear or branched C₁-C₁₈ alkyl residue, C₁-C₁₈ alkenyl residue, C₅-C₂₈ cycloalkyl residue, C₅-C₂₈ cycloalkenyl residue as well as a C₆-C₂₈ aryl residue or C₇-C₂₈ aralkyl residue

and

n denotes a number from 2.5 to 3.5,

wherein said dithiophosphoric acid polysulfide mixture is produced by reacting dithiophosphoric acid disulfides of the formula



in which

R¹ to R⁴ have the above-stated meaning,

with 0.5 to 1.5 mol of sulfur, optionally in the presence of a solvent, at temperatures of 100 to 140°C.

**PROCESS FOR THE PRODUCTION OF DITHIOPHOSPHORIC ACID
POLYSULFIDE MIXTURES**

ABSTRACT OF THE DISCLOSURE

This invention relates to a process for the production of dithiophosphoric acid polysulfide mixtures, which is characterized in that dithiophosphoric acid disulfides are reacted with sulfur at elevated temperatures. The dithiophosphoric acid polysulfide mixtures produced using the process according to the present invention are used as sulfur donors for the vulcanization of natural and synthetic rubbers and in the latex vulcanization of natural and synthetic rubber latex.

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**PROCESS FOR THE PRODUCTION OF DITHIOPHOSPHORIC ACID
POLYSULFIDE MIXTURES**

the specification of which is attached hereto,

or was filed on _____ as

Application Serial No. _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

19906986.7
(Number)

Germany
(Country)

February 19, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

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(Filing Date)

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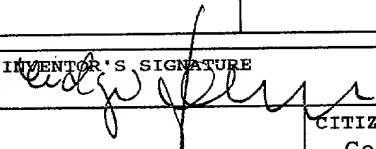
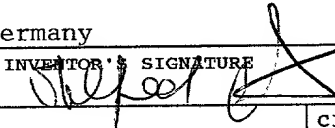
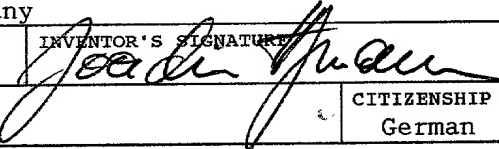
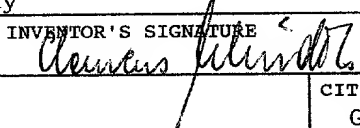
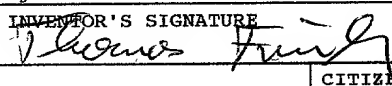
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